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TOXIC METAL REMOVAL FROM ELECTROPLATING WASTEWATER USING SILYLA--ETC(U)
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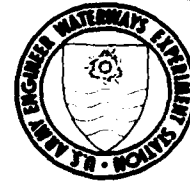
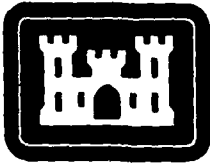
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TOXIC METAL REMOVAL FROM ELECTROPLATING WASTEWATER USING SILYLATED SILICA GEL

by

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Environmental Laboratory

U. S. Army Engineer Waterways Experiment Station

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20. ABSTRACT (Continue on reverse side if necessary and identify by block number) A preliminary study was undertaken to evaluate the usefulness of silylated silica gel in removing toxic metals from electroplating wastewater. A number of complexing and chelating systems immobilized on silica gel are available. Most involve relatively complicated syntheses, produce materials that are not stable at room temperature for long periods of time, or have very low metal removal capacities. An immobilized diamine produced from N-(ε-aminoethyl)-γ-aminopropyl-trimethoxysilane was found that could be prepared using a simple procedure (Continued)		

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and could be stored at room temperature without deterioration. Samples of material prepared in the laboratory could remove 22-24 milligrams of copper per gram of silica gel. Small-scale column studies using samples of electroplating wastewater showed that levels of cadmium, chromium, copper, nickel and zinc could be reduced significantly. Cost estimates based on the coating system used in this study show that 12.4 cents worth of silane are required to remove one gram of copper. Theoretically, the costs could be reduced to 5.2 cents per gram of copper removed. Metals removed on immobilized diamine can be recovered by stripping the silica gel column with strong oxidizing acid. The diamine coating can be replaced by treating the silica gel with additional silane. The stability, ease of preparation, and ability to recover metals make immobilized diamine a useful system for electroplating wastewater treatment.

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PREFACE

This paper reports the results of an evaluation of a metal removal system for electroplating wastewater that is based on an immobilized complexing agent on a silica gel substrate. The silica gel based system offers some significant advantage over currently used metal removal systems.

The report was prepared by Dr. Philip G. Malone, Water Supply and Waste Treatment Group (WSWTG) and Richard A. Karn, Analytical Laboratory Group (ALG). Analyses were performed by Charles White (ALG). Immediate supervisors on the project were Norman R. Francingues C/WSWTG and Ann B. Strong C/ALG. Overall direction came from Andrew J. Green, Chief of Environmental Engineering Division and Dr. John Harrison, Chief of the Environmental Laboratory. Director of the WES during this project was COL Tilford Creel, CE. Technical Director was Mr. F. R. Brown.



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PART I: INTRODUCTION

Pollution Problems from Electroplating Wastes

1. In the fabrication or refitting of Army equipment it is often necessary to plate metals in order to produce a wear-resistant, corrosion-resistant surface. The wastewater from electroplating operations contains mixtures of metals at concentrations that are potentially toxic. Some of these metals bioaccumulate in agricultural products and hence have toxic effects in the food chain even if they are discharged into the environment at very low concentrations. The problems related to these toxic metal wastes are generally more persistent than those associated with many organic wastes.

2. When electroplating wastes are introduced into conventional wastewater treatment facilities that are designed for reduction of organic waste and suspended solids, toxic metals can: (a) inhibit biological treatment processes causing the treatment plant to stop functioning or operate poorly, (b) pass through the plant and appear in the discharge water; or (c) be partially removed from the wastewater and appear as contaminants in the sewage plant sludge. None of the pathways are acceptable. The U. S. Environmental Protection Agency (1981) has examined the problem and has determined that removal of electroplating metals in wastewater treatment plants is a very ineffective process compared to specialized treatment systems (Table 1).

Table 1
Comparison of Toxic Metal Removal in a Conventional Wastewater Treatment System and the Best Available Technology for Treatment

Treatment	Removal (percent)					
	Cr	Cu	Ni	Zn	Pb	Cd
Conventional treatment	73	77	39	76	73	46
Best available technology	99	97	98	98	95	93

3. Additional problems arise from heavy metal contaminants appearing in sludge. Wastewater treatment plant sludges are routinely disposed of by land application. In land application, biological activity can reconcentrate toxic metals to harmful levels. Lead and cadmium have proved to be particularly troublesome in food contamination in sludge-treated, agricultural lands. The problem has become severe enough for the waste disposal regulations to limit the amount of contaminated wastewater sludge that can be applied to farmland.

4. Regulations have addressed the limitations to be placed on discharges from electroplating activities. Table 2 summarizes current effluent limitations. Dilution of wastewater to lower metal concentrations is not permitted. The strict control of toxic metal levels in discharged water at the industrial operations has increased the problems related to industrial waste treatment sludges. The toxic metals are now concentrated in metal hydroxide sludges that must be recycled or safely disposed.

Table 2
Regulatory Limits on Effluent from Electroplating Operations

Metals	Maximum Conc. for 1 Day* (mg/l)	Average Conc. for 4 Consecutive days (mg/l)
Cd	1.2	0.7
Cu	4.5	2.7
Cr	7.0	4.0
Ni	4.1	2.6
Pb	0.6	0.4
Zn	4.2	2.6

* Limits apply to facilities discharging more than 38,000 litres per day. From U. S. Environmental Protection Agency, 1981.

Recycling of plating metal is the most attractive option. However, most metal recovery systems are complex and energy intensive. Generally simple metal recovery systems have not retrieved the plating metal in a form that is usable in the plating plant. Metal sulfide precipitates and metal hydroxide precipitates require extensive processing to bring

the metal out in a useful form. Often the solutions are so dilute that conventional precipitation reactions do little to extract the metal.

Wastewater from Electroplating Operations

5. Wastewater from typical electroplating operations includes spent processing solutions (spent plating baths), rinse water or drag-out (diluted plating baths produced by rinsing finished parts) and clean-up water from spilled process solutions (Nemerow 1971). Metals are also contributed by the plating equipment itself, dissolution of anodes and plating tanks, and corrosion of piping carrying solutions from one part of a plant to another. Typically, an electroplating wastewater treatment plant treats three streams:

- a. A cyanide plating wastewater.
- b. A chromium-bearing wastewater.
- c. Solutions of acid, alkali and non-chromium, non-cyanide plating operations.

6. Plating wastes vary greatly from plant to plant and process to process. Generally, the cyanide-bearing wastes are treated to destroy the cyanide; this is usually done by adjusting the pH to 11 and adding chlorine with violent agitation (Figure 1). Up to twenty-four hours of chlorine treatment is necessary to assure complete cyanide oxidation. The chromium-rich wastewater is treated by reducing the Cr^{+6} to Cr^{+3} . Acid is added to reduce the pH to 3 or lower. Reducing agents such as FeSO_4 , SO_2 or NaHSO_4 are added and when the reduction is complete, the chromium is precipitated with a lime slurry (Figure 2). The sludge formed consists primarily of $\text{Cr}(\text{OH})_3$. The non-cyanide, non-chromium acid waste stream is usually neutralized with lime slurry and the resulting metal hydroxides form a heavy floc that is separated by precipitation (Figure 3). The three waste streams are generally combined on discharge.

Limitations of Current Treatment Systems

7. A typical treatment system using hydroxide precipitation has

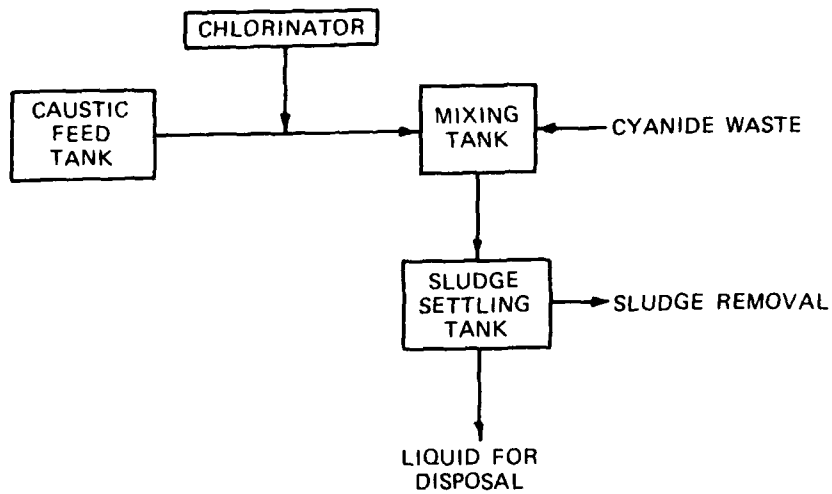


Figure 1. Process train for treating cyanide-bearing wastes

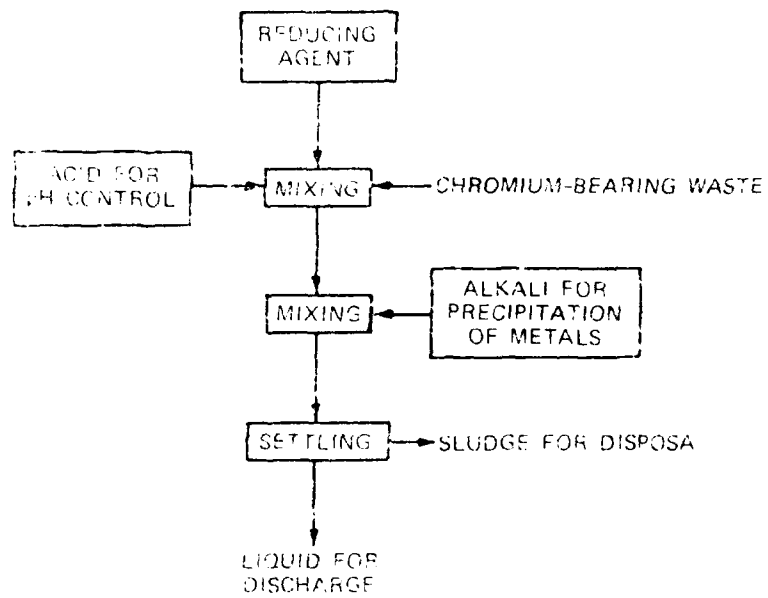


Figure 2. Process train for treating chromium-bearing wastes.

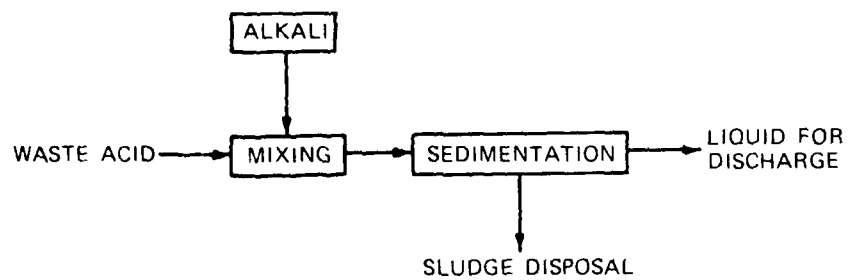


Figure 3. Process train for treating acid wastes

level. (1) Only a few of the other values presented in Table 3.

Table 3
Ranges of Concentrations of Toxic Metals Found in Electroplating
Effluent Treated with Hydroxide Precipitation

<u>Metal</u>	<u>Range of Concentrations</u> <u>(mg/l)</u>
Cadmium	Undet.* - 1.0
Chromium (trivalent)	1.06 - 0.75
Chromium (total)	0.06 - 4.6
Copper	Undet. - 2.5
Nickel	0.09 - 1.9
Zinc	0.02 - 5.4

* Undet. = Undetectable with conventional analytical systems.
From Robinson, 1978.

Comparing Table 1 and Table 3 demonstrates that typical concentration ranges in hydroxide treatment effluent may exceed the legally permissible levels. The problem involved in hydroxide precipitation occurs because the heavy metals being removed do not precipitate most efficiently at the same pH. Adjusting the pH for the minimum solubility of one metal hydroxide may result in appreciable concentrations of other metals remaining in solution. Table 4 shows the pH at minimum solubility

Table 4
Theoretical Minimum Solubilities of Metal Hydroxides
and the Corresponding Solution pH

<u>Metal</u>	<u>Theoretical</u> <u>Minimum Solubility (mg/l)</u>	<u>pH</u>
Cadmium	3.6×10^{-11}	11.0
Chromium	2.0×10^{-12}	8.5
Copper	2.5×10^{-14}	9.0
Lead	4.1×10^{-11}	9.3
Nickel	9.0×10^{-14}	10.5
Zinc	6.6×10^{-12}	9.0

for a number of metal hydroxides and the theoretical minimum concentration for selected metal hydroxides (Robinson 1978). Many metals are amphoteric, that is they are soluble at very high and very low pH's. Figure 4 shows the characteristic U-shaped curves that relate metal concentration and solution pH. For example, in plating wastewater treatment if the pH is raised to 11 (Table 4) to obtain the maximum reduction of cadmium concentration, the chromium, zinc and copper concentrations will be higher than desired.

8. The limitations on hydroxide precipitation of toxic metals have been well documented and systems for improving the effluent quality through additional metal removal by precipitation, adsorption or ion-exchange have been proposed (Robinson 1978; Stinson 1978, Blythe et al. 1981). Almost all systems involve increasing the complexity of the treatment system. For example, precipitation of metal sulfides involves the addition of equipment to add and mix sodium sulfide to the wastewater. This is a toxic compound that must itself be removed from the wastewater after reaction. Carbon adsorption columns have been proposed; but not all metals are removed by one type of activated carbon and regeneration of the adsorber and recovery of the metals have presented significant problems.

9. Immobilized chelating systems have shown great promise; but the major system currently in operation involves the use of insoluble starch xanthate (Wing 1978). The starch base for this material generally results in an easily degraded material that must be prepared and used relatively rapidly. The sludges generated may not be stable enough biologically to be a safe product for disposal.

10. The purpose of this report is to outline the basis for another metal chelating system using chelators immobilized on silica gel or a silicate base that would have superior properties for metal recovery and recycling. These materials have a surface coating of chelating material that can be stripped off to provide metal solutions that can be easily processed or even reused directly. The chelating layer can be replaced and the system put back in operation. This procedure is different from conventional precipitation or adsorption removal systems.

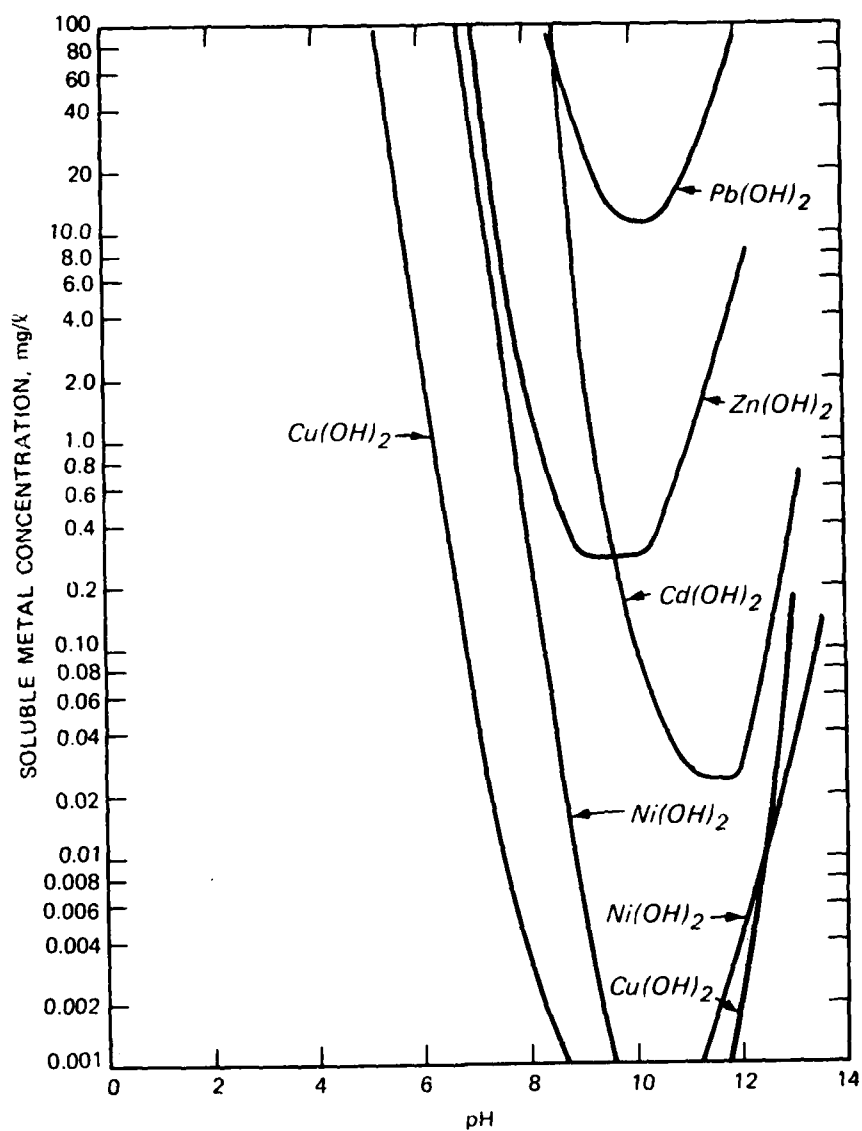


Figure 4. Theoretical solubilities of metal hydroxides
(After Robinson 1978, Blythe et al. 1981)

PART II: USE OF IMMOBILIZED REAGENTS FOR CONCENTRATION
AND REMOVAL OF METALS

General Approaches to Use of Chelating Compounds

11. A number of different approaches have been employed in concentrating metals using organic compounds. In most cases organic compounds forming complex ring structures binding the metal through intermediate nitrogen, oxygen or sulfur atoms (referred to as chelate compounds) are employed. The chelates are immobilized by trapping the organic molecule in an organic polymer such as polyurethane or in organic gels such as styrene-divinylbenzene gels. A more stable system can be obtained if the chelating compound is chemically bonded to a substrate rather than entrapped (Leyden and Wegscheider 1981).

12. Two immobilized chelating systems have been proposed for use in wastewater treatment. Lee and Davis (1973) tested a metal removal system using immobilized ethylenediaminetetraacetic acid complex on a cellulose acetate phthalate base. This material removed metal very well, but was complicated to prepare, unstable at high and low pH's and could be regenerated only by treatment with potassium thiocyanate or potassium cyanide. Wing (1978) proposed a system of metal removal based on insoluble starch xanthate (ISX). This is a highly cross linked starch treated with carbon disulfide to produce an immobilized chelator. The ISX material is easy to prepare, but has limited stability and can produce toxic decomposition products. ISX is currently being used in waste treatment.

Silylated Chelating and Complexing Agents

13. Silylation reactions bonding organic compounds to silicate substrates have proved valuable in preparing immobilized chelating agents for concentration and analysis of metals in solution. Many of these systems are rugged and relatively simple to prepare. An organo-silica compound (silane) is reacted with a glass or silica gel surface to produce bonding. The bonded silane can be a chelating group or can be

modified to form a chelating group.

14. Hercules et al. (1973) demonstrated that silylated coating on glass fiber could be modified to form a "two dimensional" ion exchanger. Glass fibers were cleaned and coated with an amino functional silylizing reagent. The coating was reacted with carbon disulfide and sodium hydroxide to form dithiocarbamate. The metal solution to be analyzed was passed through the fiber mat and the thiocarbamate group selectively reacts with heavy metals as a chelating agent. The metal levels in the coating were measured using electron spectroscopy, a technique normally used for the study of surficial bonding. The detection limit for lead, cadmium, thallium and mercury was near 10 ppb. The binding between the glass surface and metals is so strong that the technique should be useful for heavy metals in the parts-per-trillion range.

15. Sugawara et al. (1974) developed a technique for attaching 8-hydroxyquinoline to a special controlled pore glass. The glass has a relatively low surface area, 80 sq metres/gm. The glass was silanized with γ -aminopropyl triethoxysilane. The coated glass was reacted with sodium nitrite and coupled to 8-hydroxyquinoline. The product, called CPG-8-HOQ, formed stable surface complexes with even small amounts of metal in solution. For example 98 percent-100 percent recovery of copper was consistently obtained at a concentration of 39 micrograms/liter. The exchange capacity for CPG-8-HOQ was relatively low, 0.057 millimol per gram of glass. It would require 280.7 grams of glass to chelate 1 gram of copper. This material has analytical application but has too low an exchange capacity for process applications.

16. Leyden and Luttrell (1975) obtained a much higher exchange capacity by using silylation reactions to immobilize chelating groups on a silica gel substrate. Silica gel has a much larger surface area than even the best porous glass. Surface areas of silica gel are approximately 750-800 sq metres/gm compared to 80 sq metres/gm for porous glass. The larger number of chelating groups that could be attached to the increased surface area provided an exchange capacity that was reported as 0.5 to 1 millimol of copper (II) per gram of silica gel. This is equal to 1 to 2 milliequivalents/gram. Further the original work of

Leyden and Luttrell was done with type G, chromatographic-grade silica gel. Type G silica gels are made for use in thin-layer chromatography and approximately 10 percent gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) is added to the material to bind the silica gel to glass plates. The gypsum would not react with the silane but would lower the effective metal-binding capacity of the mixture.

17. Leyden and Luttrell (1975) evaluated a number of different silylated chelating agents from prepared compounds including Z-6020 diamine, N, N-dialkyldithiocarbamate from XZ-2024, N-alkyl (II) dithiocarbamate of Z-6020 diamine and the bis-thiocarbamate of Z-6020 diamine. In general all of the compounds showed selective chelating properties toward heavy metals and many were useful in metal extraction (Table 5). However not all of the silylated materials are equally stable. All

Table 5
Summary of Immobilized Chelation Products Studied
by Leyden and Luttrell (1975)

Product	Source	Capacity
		(mmols of Copper per gram of Silica gel)
A-1100 amine	Union Carbide Corp.	--
XZ-2024 amine	Dow Corning Co.	--
Silyl xanthate	--	--
Z-6020 diamine	Dow Corning Co.	0.47
XZ-2024 dithiocarbamate	Dow Corning Co.	0.53
Z-6020 dithiocarbamate	Dow Corning Co.	--
Z-6020 bis-dithiocarbamate	Dow Corning Co.	0.97

immobilized complexing and chelating agents have a dual stability problem. The silanol itself can be hydrolyzed by strong acids or bases. This strips the complex off of the silica gel substrate. However, this was not apparent as a problem at pH's ranging from 1.5 to 10.5. The second stability problem relates to the decomposition of the functional group. The diamine compound showed no evidence of degradation except

when the materials were heated for over an hour at a temperature of 150°C or higher. The immobilized diamine complexes are stable in air and can be stored at room temperature. The dithiocarbamates are unstable and must be stored under refrigeration and are easily oxidized by air. Below pH 2.5, the dithiocarbamate solutions rapidly become cloudy. Leyden and Luttrell (1975) attribute this to the decomposition of the compound and the release of carbon disulfide, a very toxic product.

18. All of the immobilized chelating and complexing materials studied by Leyden and Luttrell (1975) had capacities ranging from 0.5 to 1.0 millimol per gram of silica gel. Both the diamines and dithiocarbamates have very little affinity of alkali or alkali earth elements and these ions do not compete for functional sites.

19. All chelating and complexing groups are pH-dependent. Each metal/functional group pair has a range of optimum pH's for optimum stability. Three general groups of ions can be recognized in developing metal extraction procedures. One group, Hg (II), Cu (II) and Fe (III), will be 50 percent extracted below pH 5.0. A second group consisting of Zn (II), Ag (I), Ni (II), Pb (II) and Cd (II) will be 50% extracted at pH's between 5 and 7. A third group, Cr (III), Co (II) and Mn (II), will be 50 percent extracted in the range from pH 7.0 to 9.5.

20. Metal ion uptake rates are affected by solution pH. The diamine extracts copper (II) and mercury (II) rapidly (90 percent in less than 3 minutes at pH 7.0). Manganese (II) and chromium (III) take longer (90 percent in 17 and 22 minutes, respectively). The dithiocarbamates will extract 90 percent of all copper (II), mercury (II), manganese (II) in less than 4 minutes at pH 7.0; chromium (III) required 40 minutes to achieve 90 percent extraction. Where rates are critical, dithiocarbamates are faster in extracting all heavy metal ions except chromium (III).

Selection of Silylated Product for Evaluation

21. Any silylated material selected for metal removal in electroplating wastewater should be stable under a broad range of temperature and pH conditions. It should be easily settlable for batch operations

or capable of being used in a column. Further the material should be easily prepared from available materials and should add no toxic constituents to the wastewater. The capacity for metal removal should be as large as possible and the rate of removal must be large enough to make batch or column operations reasonable. The system should be selective for removal of toxic metals, but not extremely pH sensitive.

22. After examining the silica-based systems available, the immobilized diamine met the specifications best. The immobilized dithiocarbamates are relatively unstable and release carbon disulfide on decomposition. Carbon disulfide is highly toxic and the vapor is extremely explosive in air (it can be ignited by hot steam pipes). This compound could present serious problems in a waste treatment plant.

23. The immobilized hydroxyquinoline involves a complex synthesis and decomposed in solutions above pH 7.0. (Sugawara, Weetall and Schucker 1974). Silyl xanthates were not considered because they undergo acid hydrolysis in water and at high pH values (over 7.0) metals are removed by hydroxide complex formation in solution (Leyden and Luttrell 1975).

24. The immobilized diamine is stable in air at room temperature. Decomposition has only been noted if the material is held at 150°C for over an hour. Immobilized diamines are stable in water from pH 1.5 to pH 10.5. Strong oxidizers in solution, however, can degrade the functional groups. The capacity of the diamine is reported as 0.5 millimol per gram for copper or zinc. There are no toxic decomposition products associated with the silane and it can be stripped from the silica gel with strong acids or bases.

25. Synthesis of the diamine is an uncomplicated process that requires only a mixer and a chemical fume hood. The only product given off during the preparation of the immobilized diamine is methanol. If oven curing is required, the oven should be ventilated and equipped to handle an explosive mixture of methanol in air. Air-curing can be done in a fume hood.

PART III: EVALUATION OF IMMOBILIZED DIAMINE

Preparation of Immobilized Diamine

26. Ten batches of diamine bonded to silica gel were prepared in this study using two different silica gels and varying amounts of silylating agent (Table 6). The purpose was to determine if the grade or purity of the silica gel or the ratio of silylating agent altered the metal-binding capacity of the final product. The procedure for preparing the silylated silica gel was adapted from Leyden and Luttrell (1975) and from manufacturers product literature for the silane (Dow Corning Corp. 1979). The procedure involved only five steps:

- a. A 10 percent solution of N-(β -aminoethyl)- γ -aminopropyltrimethoxysilane (Dow Corning Z-6020) was prepared by adding the silane to water with vigorous stirring.
- b. The silane solution was acidified to pH 5 by adding reagent grade glacial acetic acid. This was checked using pH paper. Silanes can ruin pH electrodes.
- c. Clean, dry silica gel was added in varying amounts and the mixture was allowed to stir for 15 minutes using a magnetic stirrer. Polyethylene and fluorocarbon labware was used to avoid reactions with glass.
- d. The mixture was placed in a vented oven at 80°C to dry for 12 hours.
- e. The silylated silica gel was then washed with distilled deionized water, air-dried at room temperature and stored in sealed plastic bottles.

27. This procedure can be varied in many ways without altering the basic reaction. A larger quantity of more dilute (down to 0.1 percent silane) solution can be used. The pH can be adjusted anywhere in the range 3.5 to 6 using either acetic or oxalic acid. The material can be dried in air or at temperatures up to 121°C (Dow Corning Corp. 1979).

Determination of Metal Removal Capacities of Immobilized Diamine

28. Metal removal capacities were determined by reacting the known weights of different silylated silica gel preparations with a

standard copper solution, then washing off the copper solution and eluted copper-loaded silica gel with a strong solution of (4M) hydrochloric acid that hydrolyzed the silane and removed the copper. In each case 32 ml of 100 ppm CuCl_2 at pH 6.0 was added to 0.10 ± 0.01 gram of air-dried silylated, silica gel. The silica gel and standard copper solutions were initially stirred and then allowed to react for 60 minutes. The suspension was filtered through Whatman No. 1 filter paper. The silica gel was washed on the filter paper with distilled water and then eluted with 4M hydrochloric acid. The elutriate was diluted to 100 ml in a volumetric flask and the solution was analyzed for copper using a DC argon plasma emission spectrophotometer. The capacities determined for different types of silica gel treated with different amounts of silane are given in Table 6.

Table 6
Samples of Silylated Silica Gel Prepared for Evaluation

<u>Starting Material</u>	<u>Proportion of Silica Gel to 10% Silane Solution</u>	<u>Capacity Milligrams Cu/Gram of Silica Gel</u>
Chromatographic	1g:10 ml	17.9
Grade Silica Gel*	2.5g:10 ml	18.8
	5g:10 ml	23.9
	5g:10 ml	21.7
	7.5g:15 ml	21.5
Reagent Grade**	3g:10 ml	12.3
Grade Silica Gel	3.5g:10 ml	12.5
	4.0g:10 ml	8.53
	4.5g:10 ml	22.0
	5.0g:10 ml	10.6
	6.0g:10 ml	24.3

* Woelm Silica Gel 100-200 micro-meters, 70-150 mesh, Woelm Pharma, West Germany.

** Fisher Silica Gel Reagent ACS 28-200 mesh Desiccant designation, Fisher Scientific Co., Fairlawn, N. J.

29. The results indicate that the highest capacities are obtained when the proportion of silica gel to silane solution was five or six grams to 10 ml. Leyden and Luttrell (1975) reported the optimum loading was obtained with type G (10 percent gypsum) silica gel when five grams of silica gel was treated with 10 ml of silane solution. The maximum capacity observed by Leyden and Luttrell (1975) in this system was 29.8 milligrams Cu/gram of silica gel. The maximum loading found in the present study was 24.3 milligrams Cu/gram. The silica gel could not be dried to a constant weight before reacting with copper; the difference in the maximum capacities could be due to the varying amounts of moisture in the silica gel samples. Silica gel absorbs water rapidly in moist air.

30. Samples prepared with large amounts of silane in relation to the amount of silica gel had generally lower capacities suggesting that the surface of the silica gel can be coated over and the chelating groups are inhibited. Leyden and Luttrell reported that with excess silane available, a silanol polymer formed that had to be rinsed away with water. Polymer formation that blocks the silica gel pore may be a mechanism that reduces the silica gel capacity for metal uptake.

Evaluation of Metal Removal Efficiency of Immobilized Diamine in Wastewater

31. Test columns were set up to evaluate the effectiveness of immobilized diamine in removing toxic metals from an actual electroplating wastewater. Electroplating wastewater and wastewater treatment sludge were obtained from the hydroxide treatment plant at Anniston Army Depot, Anniston, Alabama. The pH of the water and suspended sludge was adjusted to a suitable range (pH 7.0 or pH 8.9) with hydrochloric acid and the slurry was filtered through Whatman No. 41 filter paper. The filtrate was tested for hexavalent chromium using the standard 1, 5-diphenylcarbohydrazide method (Hach Chemical Co., 1978). Sodium sulfite was added to the filtrate until hexavalent chromium was not detected. The concentrations of toxic metals in the filtrate varied with the pH adjustment made on the sludge suspension. Two 2-liter samples of

wastewater were made up with pH's of 7.0 and 8.9, respectively.

32. Columns of diamine were prepared in standard 12-mm-diameter glass burettes. Each column was packed with glass wool and 25 ml of silylated chromatographic-grade, silica gel (treated with 10 ml of silane to each 5 grams of silica gel). Each column contained 17.3 grams of silica gel that had a capacity of 21.5 milligrams of copper per gram. The flow rate through the columns was maintained at approximately 1 ml per minute. The analyses of the wastewater after passing through the columns are presented in Tables 7 and 8.

33. At pH 7, the diamine was ineffective in removing nickel (but removed cadmium, chromium, copper and zinc quantitatively). At pH 8.9, the diamine effectively removed cadmium, chromium, copper, nickel and zinc down to the part-per-billion level. This pH selectivity was noted by Leyden and Luttrell (1975). The best performance for a broad range of metals would be at a pH near 9.0. Most metals studied by Leyden and Luttrell (1975) showed over 90 percent removal at this pH. More complete

Table 7
Analyses of Wastewater Before and After Passing
Through the Diamine Column (pH 7.0)

Sequence of 25-ml Aliquots Passing Through Column	Element					
	Cd (mg/l)	Cr (mg/l)	Cu (mg/l)	Ni (mg/l)	Pb (mg/l)	Zn (mg/l)
1st	0.035	0.024	0.006*	0.198	CI	0.073
2nd	0.025	0.005	0.003	0.144	CI	0.014
3rd	0.088	0.008	0.004	0.126	CI	0.015
4th	0.140	0.101	0.004	0.124	CI	0.012
5th	0.180	0.229	0.003	0.127	CI	0.027
Wastewater (pH 7)	0.270	0.453	0.046	0.146	CI**	0.189

* Values below 0.01 ppm are considered approximate because they are below the usual reporting level for plasma emission.

** CI = Chemical interference.

Table 8
Analyses of Wastewater Before and After Passing
Through the Diamine Column (pH 8.9)

Sequence of 25-ml Aliquots Passing Through Column	Element					
	Cd (mg/l)	Cr (mg/l)	Cu (mg/l)	Ni (mg/l)	Pb (mg/l)	Zn (mg/l)
1st	0.002*	0.001	0.011	0.003	0.001	0.003
2nd	<0.001	<0.001	0.003	0.009	0.080	0.005
3rd	0.020	0.228	0.003	0.139	0.024	0.006
4th	0.060	0.699	0.002	0.113	0.013	<0.001
5th	0.116	0.722	0.002	0.116	0.009	<0.001
6th	0.152	0.748	0.002	0.115	0.006	0.003
Wastewater (pH 8.9)	0.287	1.80	0.074	0.143	CI**	0.285

* Values below 0.01 ppm are considered approximate, because they are below the usual reporting level for plasma emission.

** CI = Chemical interference.

removal in this study could have been achieved if the contact time or residence time in the column was increased. The residence time in the column tests was approximately 10 minutes. Published data indicate that 22 minutes was necessary to assure 90 percent removal (at pH 7.0) of the slower reacting cations such as chromium.

34. The column tests indicate that the diamine can be successfully applied to a complex mixture of metals. The system reduces metal concentrations down to drinking water levels for cadmium, chromium, copper, nickel and zinc. This is far below the levels required for conventional electroplating waste treatment.

PART IV: TREATMENT SYSTEMS USING IMMOBILIZED DIAMINE

Use of Silylated (Diamine) Silica Gel in the Treatment of Electroplating Wastewater

35. Silylated (diamine) silica gel has unusual properties as a wastewater cleanup material and can be employed in several innovative ways. Most metal removal systems do not extract metals efficiently at low (less than 10 ppm) concentrations; silylated silica gels work very well at those levels because of their great affinity for metals. Most systems will not release metals in a useable, concentrated form. Silylated silica gels have the advantage that the silane can be destroyed with a strong, oxidizing acid and the metal is released, while the support, silica gel, is not disturbed, and can be recoated. The metal in a concentrated solution can be processed to produce more plating bath.

36. The most cost effective system for using silylated silica would be metal removal from very dilute metal solutions such as rinse water used to clean plating solution off of finished parts. For example, in an acid copper plating operation, a silica gel column could be used to reconcentrate the dilute copper solution (100 ppm Cu) developed in rinse water used to wash copper sulfate off of plated parts. A copper-free solution could be recycled for rinsing and the copper on the column could be removed (periodically) with a small volume of strong sulfuric acid solution. The resulting concentrated copper sulfate solution would be available for addition to new plating baths. This allows more copper to go out in the plated product and less as hazardous waste sludge and reduces the amount of clean water needed for rinsing. The volume of water requiring final treatment and discharge is also correspondingly lowered. The advantage for the silylated silica gel system would come from more efficient metal use and a reduction in the volume of rinse water that had to be processed in the main treatment facility.

37. In operations where a copper part is being acid etched prior to plating it would normally be difficult to reclaim or reuse metal from a spent acid etch. With a silylated silica gel column, the solution

could be adjusted to a suitable pH (pH 5 or above) and the copper could be selectively extracted and concentrated on a silica gel column.

38. If costs for the silylated silica products were low enough, it would also be possible to use silylated silica materials directly against concentrated metal wastewater and even to discard (after suitable solidification) the metal loaded silane and silica. It is possible to attach a diamine silane compound to any silica or alumina surface that has active (-OH) sites (Arkles 1977); therefore, inexpensive supports such as flyash or clay could be employed to make a use-and-discard system. If coating techniques could be made more efficient and all of the diamine silane formed an accessible monolayer, the silane could bind approximately 28 percent of its weight in copper. When used in bulk, silylated silica materials can reduce toxic metal levels below present discharge standards.

Economic Considerations in the Use of Silylated (Diamine) Silica Gel

39. The least expensive component in a silica gel system is the silica gel itself. When furnished in 200 kg lots the material cost \$2.20/kg (1982 price). However, the silica gel can be cleaned and regenerated; therefore the actual item consumed in the water treatment process is the silane.

40. In this preliminary investigation, a silane coating formula developed by Leyden and Luttrell (1975) was employed and silica gel products capable of removing approximately 24 milligrams of copper per gram of silica gel were obtained. This coating required approximately two milliliters of 10 percent coating solution per gram of silica gel. The amount of silane used was 0.2 gram per gram of silica gel and would cost 0.3 cent (1982 price) purchased in bulk. At this coating rate it would require 41.7 grams of silica gel to remove one gram of copper and the cost would be 12.4 cents. Theoretically the cost could be much lower. The diamine uptake of copper is a 1:1 reaction; one molecule of diamine complexes or chelates one atom of copper. Each gram of copper (atomic weight = 63.5) should require 3.5 grams of diamine (molecular

weight = 222.1). The cost would be 5.20 cents per gram of copper for the required amount of silane.

41. The metal removal system could also be much more compact than this preliminary investigation suggests. Most siliceous surfaces have enough active binding sites to hold one mol of silane on every 7500 sq metres (Arkles, 1977). Silica gels have 750-800 sq metres per gram of available surface area. Ten grams of silica gel should be able to provide active sites enough to hold 222 grams of diamine and this would be sufficient diamine to remove 63.5 grams of copper from solution.

42. The theoretical efficiency of a silylated silica gel system can be realized if the reaction between the diamine and the silica gel is carefully controlled. The untreated silica gel can be treated with dilute hydrochloric acid to assure the maximum number of active sites are produced. The silica gel can be rinsed and air dried at a relatively low temperature (105°C) and the silylating solution can be diluted to as low as 0.1 percent to assure the reacting fluid has very low viscosity. The diamine used in this study is routinely used to improve the bonding between glass fiber and plastic materials such as melamine. Product literature (Dow Corning, 1979) outlines details on mixing and reacting the silane on an industrial production scale where complete surface coating is required.

PART V: SUMMARY

43. A preliminary study was undertaken to evaluate the usefulness of silylated silica gel in removing toxic metals from plating solutions. A number of immobilized chelating and complexing systems are available; but most involve relatively complicated synthesis and result in products that are not stable at room temperature for more than a few days. Further many immobilized chelating systems have very low metal removal capacities (a few hundredths of a millimol of metal per gram).

44. The system with the best stability, easiest synthesis and a useful metal removal capacity was the immobilized diamine produced by reacting N-(β -aminoethyl)- γ -aminopropyltrimethoxysilane with silica gel. This material is marketed by Dow Corning as Z-6020 silane. A simple five-step process attached the diamine to silica gel. The resulting material had a metal removal capacity in the order of 22-24 milligrams of copper per gram of silica gel. Small test columns of silica gel were used to treat samples of electroplating wastewater from Anniston Army Depot, Anniston, Alabama. At a pH of 8.9 metal levels in the low part-per-billion range were produced in the treated water. Cadmium, chromium, copper, nickel and zinc were quantitatively removed by the silylated silica gel. The major expense in using this metal concentration or removal system is the silylating compound. The coating system used in this preliminary study was relatively wasteful and used 12.4 cents worth of silane to produce material that could remove one gram of copper from solution. Theoretically it may be possible to remove one gram of copper using only 5.2 cents worth of silane.

45. The relatively safe, stable nature of the immobilized diamine and its ability to produce a recyclable concentrated metal solution make it a very attractive pollution control and metal recovery system for electroplating wastewater. Immobilized diamine would be particularly useful in treating and concentrating metal from dilute metal solutions (approximately 100 ppm) produced by rinsing and etching operations. The immobilized diamine system has the potential for becoming one of the best removal systems available because:

- a. It offers excellent metal removal efficiency.
- b. It involves simple preparation that can be safely performed at the plating facility.
- c. It allows the metal to be recovered as a concentrated solution that can be reused.

REFERENCES

- Arkles, Barry. 1977. "Techniques for Silylation," Chemtech, Vol 7, pp 713-717.
- Blythe, M., et al. 1981. "Characterization of Boliden's Sulfide-Lime Precipitation System," EPA-600/S2-81-081, U. S. Environmental Protection Agency, Cincinnati, OH.
- Dow Corning Corp. 1979. "Information about Organofunctional Silane Chemicals-Dow Corning Z-6020 Silane," No. 23-231A-79, Midland, Mich.
- Hach Chemical Co. 1978. Water Analysis Handbook, Hach Chemical Co., Loveland, Colorado, 631 pp.
- Hercules, D. M., et al. 1973. "Electron Spectroscopy (ESCA): Use for Trace Analysis," Analytical Chemistry, Vol 45, No. 11, pp 1973-1975.
- Lee, L. A. and Davis, H. J. 1973. "Removal of Heavy Metal Pollutants from Natural Waters," Transactions of the 1973 Symposium on Trace Metals and Metal-Organic Interactions in Natural Waters, American Chemical Society, pp 363-374.
- Leyden, D. E. and Luttrell, G. H. 1975. "Preconcentration of Trace Metals Using Chelating Groups Immobilized via Silylation," Analytical Chemistry, Vol 47, No. 9, pp 1612-1617.
- Leyden, Donald E. and Wegscheider, Wolfherd. 1981. "Preconcentration for Trace Element Determination in Aqueous Samples," Analytical Chemistry, Vol 53, No. 9, pp 1059A-1065A.
- Nemerow, Nelson L. 1971. Liquid Waste of Industry: Theories, Practices, and Treatment, Addison-Wesley Reading, Massachusetts, pp 584.
- Robinson, A. K. 1978. "Sulfide-vs-Hydroxide Precipitation of Heavy Metals from Industrial Wastewater," First Annual Conference On Advanced Pollution Control for the Metal Finishing Industry, The American Electroplaters' Society and the U. S. Environmental Protection Agency, EPA-600/8-78-010, pp 59-65.
- Stinson, M. K. 1978. "Emerging Technologies for Treatment of Electroplating Wastewaters," Proceedings of American Institute of Chemical Engineers, 71st Annual Meeting (Session 69), pp 25.
- Sugawara, K. F., Weetall, H. H. and Schucker, G. D. 1974. "Preparation, Properties, and Applications of 8-Hydroxyquinoline Immobilized Chelate," Analytical Chemistry, Vol 46, No. 4, pp 489-492.
- U. S. Environmental Protection Agency. 1981. "General Pretreatment Regulations for Existing and New Sources," Federal Register, Vol 48, No. 18, pp 9401-9554.
- Wing, R. E. 1978. "Processes for Heavy Metal Removal from Plating Wastewaters," First Annual Conference on Advanced Pollution Control for the Metal Finishing Industry, The American Electroplaters' Society and the U. S. Environmental Protection Agency, EPA-600/8-78-010, pp 92-106.

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